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In the matter of an application for a German Patent in the name of Covion Organic Semiconductors GmbH, filed under No. 102 29 370.8 on 29 June 2002 and in the matter of an application for a United States Patent.

I, Dr. Ashwood Stephen DRANE, B.Sc., Ph.D., BDÜ, translator to SD Translations Ltd. of Beechwood, Chivery, Tring, Hertfordshire, HP23 6LD, England, do solemnly and sincerely declare:

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 26th day of April 2006



Dr. Ashwood Stephen Drane

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# FEDERAL REPUBLIC OF GERMANY

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## Priority certificate regarding the filing of a patent application

**File reference:** 102 29 370.8  
**Date of filing:** 29 June 2002  
**Applicant/proprietor:** Covion Organic Semiconductors GmbH,  
Frankfurt am Main/DE  
**Title:** 2,1,3-Benzothiadiazoles  
**IPC:** C 07 D, C 09 K

**The attached pages are a correct and accurate reproduction of the original documents of this patent application.**

Seal

Munich, 30 May 2003  
**German Patent and Trademark Office**  
On behalf of  
**The President**

[signature]

Weihmayr

## Description

## 5 2,1,3-Benzothiadiazoles

Organic compounds will in the near future be employed as functional components as active components (= function materials) in a number of different applications which can be ascribed to the electronics industry in the broadest sense.

10 In the case of the organic electroluminescent devices based on organic components (general description of the structure cf. US-A-4,539,507 and US-A-5,151,629) or individual components thereof, the organic light-emitting diodes (OLEDs), the market introduction has already taken place, as confirmed by the available car radios with an "organic display" from Pioneer. Further products of this type are just  
15 about to be introduced. In spite of everything, significant improvements are still necessary here in order to make these displays a true competitor to the liquid-crystal displays (LCDs) which currently dominate the market, or to surpass them.

20 Essential conditions for practical use which may be mentioned here are, in particular, a long operating lifetime, high stability to temperature stresses and a low use and operating voltage in order to facilitate mobile applications.

25 The general structure of organic electroluminescent devices is described, for example, in US 4,539,507 and US 5,151,629.

An organic electroluminescent device usually consists of a plurality of layers, which are preferably applied one on top of the other by means of vacuum methods. These layers are in detail:

1. Support plate = substrate (usually glass or plastic sheets).
- 30 2. Transparent anode (usually indium-tin oxide, ITO).

3. (Hole Injection Layer = HIL): for example based on copper phthalocyanine (CuPc), conductive polymers, such as polyaniline (PANI), or polythiophene derivatives (such as PEDOT).
4. (Hole Transport Layer = HTL): usually based on triarylamine derivatives.
5. (Emission Layer = EML): this layer may in some cases coincide with layers 4 or 6, but usually consists of fluorescent dyes or host molecules doped with fluorescent dyes.
6. (Electron Transport Layer = ETL): in most cases based on aluminium tris-8-hydroxyquinoxalinate (AlQ<sub>3</sub>).
7. (Electron Injection Layer = EIL): this layer may in some cases coincide with layer 6 or a small part of the cathode is specially treated or specially deposited.
8. Cathode: use is generally made here of metals, metal combinations or metal alloys having a low work function, for example Ca, Ba, Mg, Al, In, Mg/Ag.

This entire device is structured depending on the application, provided with contacts and finally also hermetically sealed, since the lifetime of devices of this type is generally drastically reduced in the presence of water and/or air.

On application of a corresponding voltage, holes are injected into the device from the anode and electrons from the cathode and meet in the device and produce an excited state. This can relax with emission of light. This light is emitted through the transparent anode. In some applications, it may also be appropriate to rotate the arrangement precisely, i.e. to utilise a (semi)transparent cathode if the anode is applied, for example, to a non-transparent substrate (for example a silicon switching chip).

In any case, the individual OLED will emit light which has a colour specified by the EML. In this way, it is possible to produce the three primary colours (blue, green, red), depending on the EML.

Through a suitable combination of various individual OLEDs, it is now possible to produce different types of device, starting from individual light-emitting diodes, via

simple segmented displays, via more complex matrix displays to full-colour, large-format displays/screens.

In the OLED devices explained above, the EML function materials have been or are being intensively optimised. In spite of intensive optimisation, the characteristic data of the OLEDs described above have a number of weak points, with two weak points – the short lifetime of the EML materials and the unfavourable efficiency/brightness curves – proving to be a particular hindrance in turning OLED technology into marketable products:

1) The realistic lifetime of the OLED materials available today under near-practical conditions is greatly limited. The lifetime (time after which the luminance has dropped to 50% of the initial luminance) in the red, at a constant current density and an initial luminance of  $100 \text{ Cd/cm}^2$ , is at best a few thousand hours. In the blue, by contrast, only a few hundred to at best two to three thousand hours are usually achieved at an initial luminance of  $100 \text{ Cd/cm}^2$ .

These lifetimes are inadequate for practical applications and hinder the market introduction of OLED devices.

2) It is evident from the efficiency/brightness curves of conventional materials that the efficiency drops greatly with increasing brightness. This means that the high brightnesses necessary in practice can only be achieved via high power consumption. However, high power consumptions require high battery performances of portable equipment (mobile phones, laptops, etc.). In addition, the high power consumption, which is for the most part converted into heat, may result in thermal damage to the display.

These deficiencies in the prior art give rise to the following objects:

The provision of EML materials having a long operating lifetime at industrially useful luminances, in combination with flat efficiency/brightness curves, i.e. materials which have good efficiencies even at high brightnesses.

Surprisingly, it has now been found that certain compounds which contain the 2,1,3-benzothiadiazole unit have excellent properties on use as EML (as pure substance or as dopant in a host molecule matrix).

The present invention relates to compounds which contain the 2,1,3-benzothiadiazole unit. These compounds are distinguished by the following properties:

1. The emission colour of the compounds according to the invention can be adjusted over the entire visible region, i.e. from deep blue to deep red, through the choice of a suitable substitution pattern (see examples).
2. On use in corresponding devices, the compounds containing 2,1,3-benzothiadiazole according to the invention result in excellent operating lifetimes, as shown by way of example by Example R1 and the lifetime measurement carried out therewith. Even after an operating time of 2500 hours, no significant drop in luminance is observed. This unique behaviour, due to the 2,1,3-benzothiadiazole unit, gives rise to expectations of lifetimes of  $\gg 10,000$  hours.
3. The compounds containing 2,1,3-benzothiadiazole according to the invention, employed as EML material in electroluminescent devices, result in high efficiencies therein, in particular even at the high current densities desired industrially. Very good efficiencies are thus facilitated, even at high current densities.
4. The compounds containing 2,1,3-benzothiadiazole according to the invention can be prepared in a highly reproducible manner in reliably high purity and have no batch variations.
5. The compounds containing 2,1,3-benzothiadiazole according to the invention are distinguished by high temperature stability. Glass transition temperatures of greater than  $100^{\circ}\text{C}$  are achieved through the choice of suitable substitution patterns.
6. The compounds containing 2,1,3-benzothiadiazole according to the invention have excellent solubility in organic solvents. These materials can thus also be processed from solution by coating or printing techniques. In a preferred embodiment, solutions can also be processed together with one or more other compounds, which may be either of low molecular weight or of relatively high or high molecular weight. This property is even advantageous in the case of conventional processing by evaporation since cleaning of the equipment and the shadow masks employed is thus considerably simplified.

In addition to the very good properties as EML, it has also been found, surprisingly, that certain compounds containing 2,1,3-benzothiadiazole have excellent properties on use as ETL, as HBL (Hole Blocking Layer), or as host material in the EML, and particularly as host material in novel phosphorescent OLED devices. The present invention therefore likewise relates to the use of these compounds in phosphorescent organic electroluminescent devices (general structure and functioning see: M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Applied Physics Letters, **1999**, 75, 4-6).

On consideration of the prior art in relation to ETL materials, it is striking that the ETL used in all devices is virtually exclusively AlQ<sub>3</sub>. This compound is also, as mentioned above, frequently additionally used as host material for the EML. Although it has already been attempted many times to replace this compound by other substances, this has, however, not succeeded to date. AlQ<sub>3</sub> hitherto still represents the best compromise for the various requirements. Thus, the compound, besides high thermal stability (glass transition temperature T<sub>g</sub> ~ 190°C), has an evidently usable band position and an acceptable fluorescence quantum efficiency in the solid (about 40%). However, the inherent colour (absorption: yellow) of the compound, which can result in colour shifts, especially in blue OLEDs, due to fluorescence absorption and re-emission, is negative. This only becomes a severe disadvantage in the case of the above-mentioned device structure, in which the light is emitted through the cathode, i.e. also through the ETL. Blue OLEDs can only be produced here with considerable adverse effects on efficiency and colour location.

The usability of AlQ<sub>3</sub> in the novel phosphorescent OLEDs has likewise in no way finally been clarified.

A further disadvantage of the use of AlQ<sub>3</sub> is the instability to holes, which has in the meantime been disclosed in the literature [cf., for example, Z. Popovic et al., Proceedings of SPIE, **1999**, 3797, 310-315], which can always result in problems in the device on long-term use.

A crucial practical disadvantage of AlQ<sub>3</sub> is the high hygroscopicity of this compound. AlQ<sub>3</sub>, which is synthesised and stored under standard conditions, still contains one molecule of water per complex molecule in addition to the hydroxyquinoline ligands [cf., for example: H. Schmidbaur et al., Z. Naturforsch. **1991**, 46b, 901-911]. This water is extremely difficult to remove. For use in OLEDs, AlQ<sub>3</sub> therefore has to be subjected to complex purification in complicated, multistep sublimation processes, and subsequently stored and handled in a protective-gas atmosphere with exclusion of water. Furthermore, considerable variations in the quality of individual AlQ<sub>3</sub> batches and poor storage stability have been noted (S. Karg, E-MRS Conference 30.5.00-2.6.00 Strasbourg)

For the novel phosphorescent OLEDs, on the one hand AlQ<sub>3</sub> is likewise used as ETL, on the other hand the question of the host material for the actual triplet emitter has not been clarified at all. To date, only the use of a few materials (4,4'-bis-carbazolylbiphenyl, polyvinylcarbazole, and a triazole derivative) has been reported. However, the operating lifetimes in particular are still in considerable need of optimisation.

The compounds containing 2,1,3-benzothiadiazole according to the invention, which can be used as ETL, as HBL, or as host material in the EML, are distinguished, in particular compared with AlQ<sub>3</sub> and the few host materials disclosed to date for phosphorescent OLEDs, by the following properties:

1. They are colourless or virtually colourless; this means that their UV/VIS absorption in the wavelength range between 400 and 700 nm is negligible. In electroluminescent devices according to the invention, this results in better colour purity and higher efficiency. This has the advantage that, in particular in blue OLEDs, they do not result in a colour shift or reduction in efficiency. A further advantage is naturally their use as host or ETL material, in particular in inverted (cf. above) device geometries.
2. The compounds containing 2,1,3-benzothiadiazole according to the invention – employed as host or ETL material in the electroluminescent devices according to the invention – result in high efficiencies therein, which are, in particular, inde-



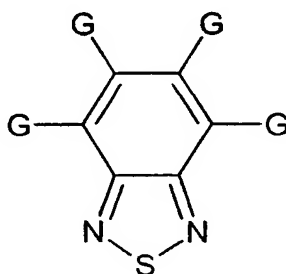
pendent of the current densities used. Very good efficiencies are thus facilitated, even at high current densities.

3. The compounds containing 2,1,3-benzothiadiazole according to the invention are distinguished by high oxidation stability. This can result in a significant increase in the operating lifetime on use in corresponding devices according to the invention. Furthermore, the production of these devices is simplified.
4. The compounds containing 2,1,3-benzothiadiazole according to the invention have no evident hygroscopicity, and have high stability to atmospheric oxygen. Storage for a number of days or weeks in contact with air and water vapour does not result in any changes to the substances. The adduction of water onto the compounds is not evident. Naturally, this has the advantage that the substances can be purified, transported, stored and prepared for use under simpler conditions. The use does not – in contrast to the operations in the case of  $AlQ_3$  – have to take place continuously under protective gas.

In addition, as described above in the case of the use as EML materials, they can be prepared reproducibly in good yields, are temperature-stable and are readily soluble in organic solvents.

The use of molecularly defined, uniform, low-molecular-weight (molecular weight < 5000 g / mol) compounds containing 2,1,3-benzothiadiazole in OLED devices is novel.

The invention relates to compounds which contain at least one structural unit of the formula (I)



Formula (I)

characterised in that the group G corresponds to hydrogen, fluorine and/or an organic radical, the compounds belong to the idealised point group  $S_n$ ,  $C_n$ ,  $C_{nv}$ ,  $C_{nh}$ ,  $D_n$ ,  $D_{nh}$  or  $D_{nd}$  where  $n=2, 3, 4, 5$  or  $6$ , the molecular weights are in the range from 450 g/mol to 5000 g/mol, the melting points are above a temperature of 190°C, and with the proviso that no macrocycle is present.

Point group here is used as a term from group theory, as described, for example, in: F. A. Cotton, Chemical Applications of Group Theory, 3rd edition, New York, Wiley, **1990**.

Macrocycle is taken to mean a ring having more than eight ring atoms (J.-M. Lehn, Dietrich, Viont, Makrocyclic Compounds Chemistry, Weinheim, VCH Verlag, **1992** and Tetrahedron **1995**, 51, 9241-9284, 9767-9822).

The compounds containing 2,1,3-benzothiadiazole according to the invention are excellently suitable for use as electroluminescent materials. They can likewise be employed as dopants in a multiplicity of host materials.

Corresponding OLED devices which contain the compounds containing 2,1,3-benzothiadiazole according to the invention have high EL efficiency as well as a long lifetime.

The prerequisite for this are the above-described properties with respect to symmetry. The compounds containing 2,1,3-benzothiadiazole must have at least one axis of rotation having a multiplicity of 2 or more, since in these cases the fluorescence quantum yield and thus the electroluminescence quantum yield is particularly great and is generally significantly greater than in the case of more asymmetrical compounds of point groups  $C_1$  and  $C_s$ .

A further necessary prerequisite that suitable OLED materials have to satisfy, in particular if applied via vacuum evaporation or evaporation in a stream of carrier gas, is a molecular weight in the range from 450 g/mol to 5000 g/mol. In the case of a molecular weight below that mentioned above, the vapour pressure is so great,

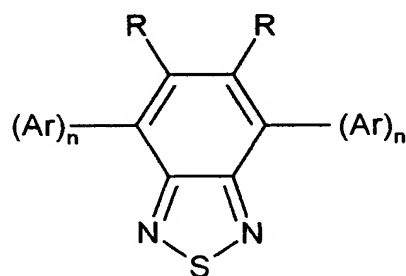
even at low temperatures, that the vacuum units are massively contaminated. On the other hand, experience shows that if the upper molecular weight limit is exceeded, decomposition-free evaporation is no longer possible.

Closely linked to the molecular weight are the melting points of the compounds. These must be approximately above 190°C since only then is adequately slow and uniform evaporation ensured and only this results in homogeneous, glass-like films. However, glass-like films are a vital prerequisite for functioning OLEDs. The melting point of a compound is given by the temperature at which the phase transition from the solid state into the liquid state occurs.

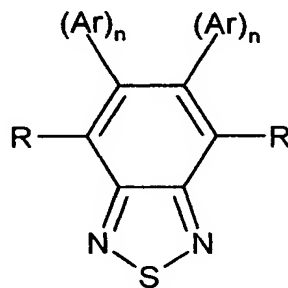
In addition, an adequately high glass transition temperature – in the region above 100°C – is a necessary prerequisite for OLEDs which are stable in the long term. Experience shows that the glass transition temperature in the case of suitable organic materials is typically at least 60°-90°C below the melting point, and consequently a melting point of 190°C also represents a lower limit in respect of this property.

In addition, the compounds containing 2,1,3-benzothiadiazole must not have a macrocyclic structure since otherwise they efficiently complex the palladium used during the synthesis and thus deactivate the coupling catalyst. In addition, these complex compounds can only be separated quantitatively from the product with difficulty, meaning that purification of the corresponding compounds is no longer possible in an efficient manner.

The invention likewise relates to compounds of the formula (II) and (III)



**Formula (II)**



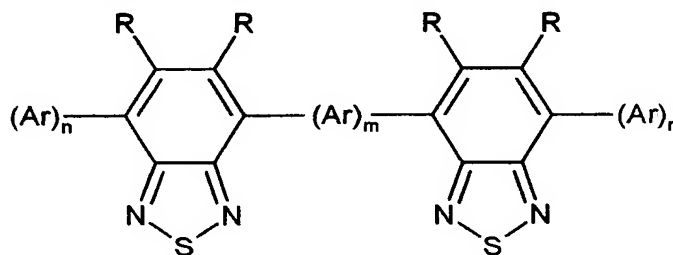
**Formula (III)**

where the symbols and indices have the following meaning:

- R** is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -NR<sup>1</sup>-, or -CONR<sup>2</sup>- and in which one or more H atoms may be replaced by F;
- Ar** is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;
- R<sup>1</sup>, R<sup>2</sup>** are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;
- n** is equal to 1 to 10, preferably 1 to 6, particularly preferably 1, 2 or 3.

Depending on the choice of the substituents Ar, the property profile of the above-mentioned compounds of the formula (II) or (III) can be customised with respect to the property profile required for OLED applications. Thus, the emission colour can be adjusted specifically over the entire visible region from deep red to deep blue, for example through the suitable choice of the substituent Ar (see examples).

The invention likewise relates to compounds of the formula (IV)



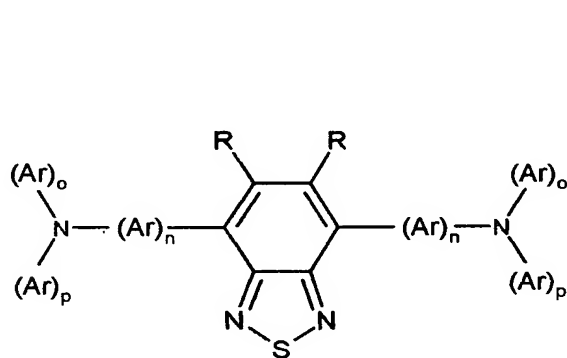
**Formula (IV)**

where the symbols and indices R, Ar, R<sup>1</sup>, R<sup>2</sup> and n have the above-mentioned meaning and m has the following meaning:

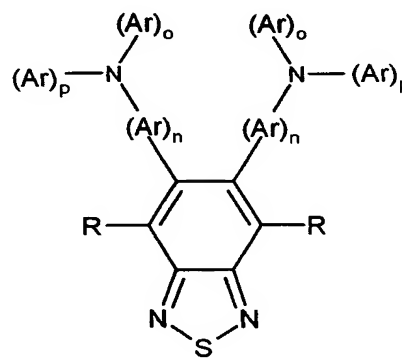
- m** is equal to 0 to 4, preferably 1 or 2;

A repetitive concatenation of conjugatively isolated, emitting sub-units, which is achieved, inter alia, through multiple repetition of 2,1,3-benzothiadiazole units and aromatic radicals Ar – compounds of the formula (IV) – results in materials having correspondingly shorter emission wavelength (blue emission colour) paired with a high molecular weight, which ensure the above-mentioned positive properties with respect to evaporation and the glass transition point.

Balanced charge carrier injection (hole or electron injection) into the emission layer and balanced charge carrier transport in the emission layer are the basic prerequisite for efficient OLEDs having a long lifetime. Since the compounds containing 2,1,3-benzothiadiazole, as described above, are good electron conductors, it may prove favourable in the specific individual case specifically to incorporate hole-conducting units, for example triarylamine units, as is shown in compounds of the formulae (V) and (VI), into the emitter material of the EML. Accordingly, the invention likewise relates to compounds of the formula (V) and (VI):



Formula (V)



Formula (VI)

where the symbols and indices R, Ar,  $R^1$ ,  $R^2$  and n have the above-mentioned meaning and o and p have the following meaning:

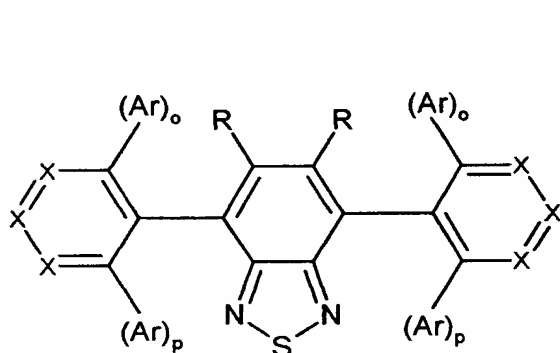
o is equal to 1 to 3, preferably 1;

p is equal to 1 to 3, preferably 1.

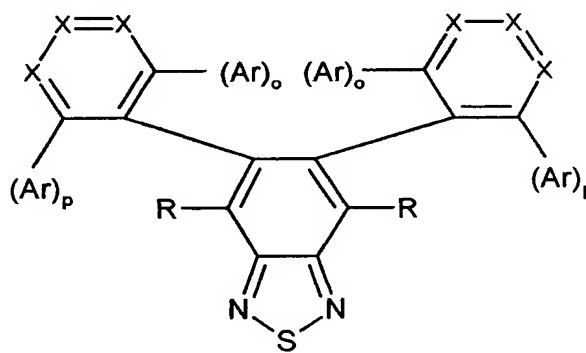
Compounds of the formula (V) and (VI), but also (VII), (VIII) and (IX), (X) and (XI) containing 2,1,3-benzothiadiazole according to the invention (see below), which are distinguished by a strong twist of the 2,1,3-benzothiadiazole unit and the linked aromatic/heteroaromatic units, have a low HOMO ( $< 5.5$  eV relative to the vacuum level) and thus pronounced oxidation stability. Accordingly, they are particularly

suitable for use as ETL, as HBL, but also as host material in the EML. Given a suitable choice of the aromatic/heteroaromatic radicals Ar, they are in addition capable, through electron-hole recombination, of generating triplet states, which can then be transferred efficiently to doped-in phosphorescent emitters. This property is particularly advantageous on use of the compounds of the formula (VII) and (VIII) host material in novel phosphorescent OLEDs.

The invention additionally relates to compounds of the formula (VII) and (VIII):



**Formula (VII)**



**Formula (VIII)**

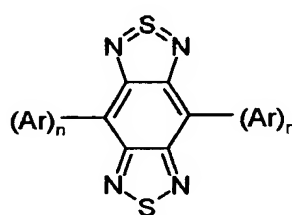
where the symbols and indices R, Ar, R<sup>1</sup> and R<sup>2</sup> have the above-mentioned meaning and X, o and p has the following meaning:

X is, identically or differently on each occurrence, C(Ar), CR or N;

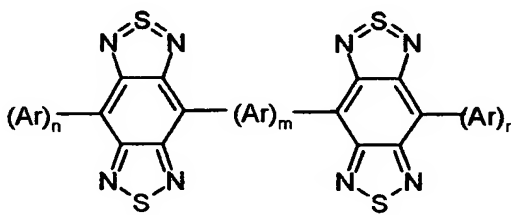
o is equal to 1 to 3, preferably 1;

p is equal to 1 to 3, preferably 1.

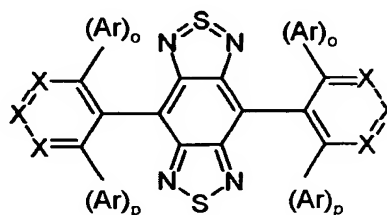
The invention additionally relates to compounds of the formula (IX), (X) and (XI):



**Formula (IX)**



**Formula (X)**



**Formula (XI)**

where the symbols and indices X, R, Ar, R<sup>1</sup>, R<sup>2</sup>, m, n, o and p have the above-mentioned meaning.

Preferred compounds of the formula (I) to (XI) are characterised in that the aryl or heteroaryl group Ar has 3 to 24 C atoms, particularly preferably 3 to 14 C atoms.

Preferred compounds of the formula (I) to (XI) are characterised in that the radical Ar stands for benzene, toluene, xylene, fluorobenzene, difluorobenzene, biphenyl, 1,2- or 1,3- or 1,4-terphenyl, tetraphenyl, naphthyl, fluorene, 9,9'-spirobifluorene, phenanthrene, anthracene, 1,3,5-triphenylbenzene, pyrene, perylene, chrysene, triptycene, [2.2]paracyclophan, pyridine, pyridazine, 4,5-benzopyridazine, pyrimidine, pyrazine, 1,3,5-triazine, pyrrole, indole, 1,2,5- or 1,3,4-oxadiazole, 2,2'- or 4,4'-bipyridyl, quinoline, carbazole, 5,10H-dihydrophenazine, 10H-phenoxazine, phenothiazine, xanthene, 9-acridine, furan, benzofuran, thiophene or benzothio-  
phene.

Although the above comments describe principally a use of the compounds containing 2,1,3-benzothiadiazole according to the invention in OLED devices, it should be pointed out that these compounds can likewise be used very well in the following devices:

1. Use as electron transport material in electrophotography.
2. Use in photovoltaic devices, such as organic photodetectors or organic solar cells, as electron acceptor or transport material.
3. Use in organic integrated circuits (O-ICs).
4. Use in organic field-effect transistors (OFETs).
5. Use in organic thin-film transistors (OTFTs).
6. Use in further applications – in some cases mentioned above – such as organic solid-state lasers.

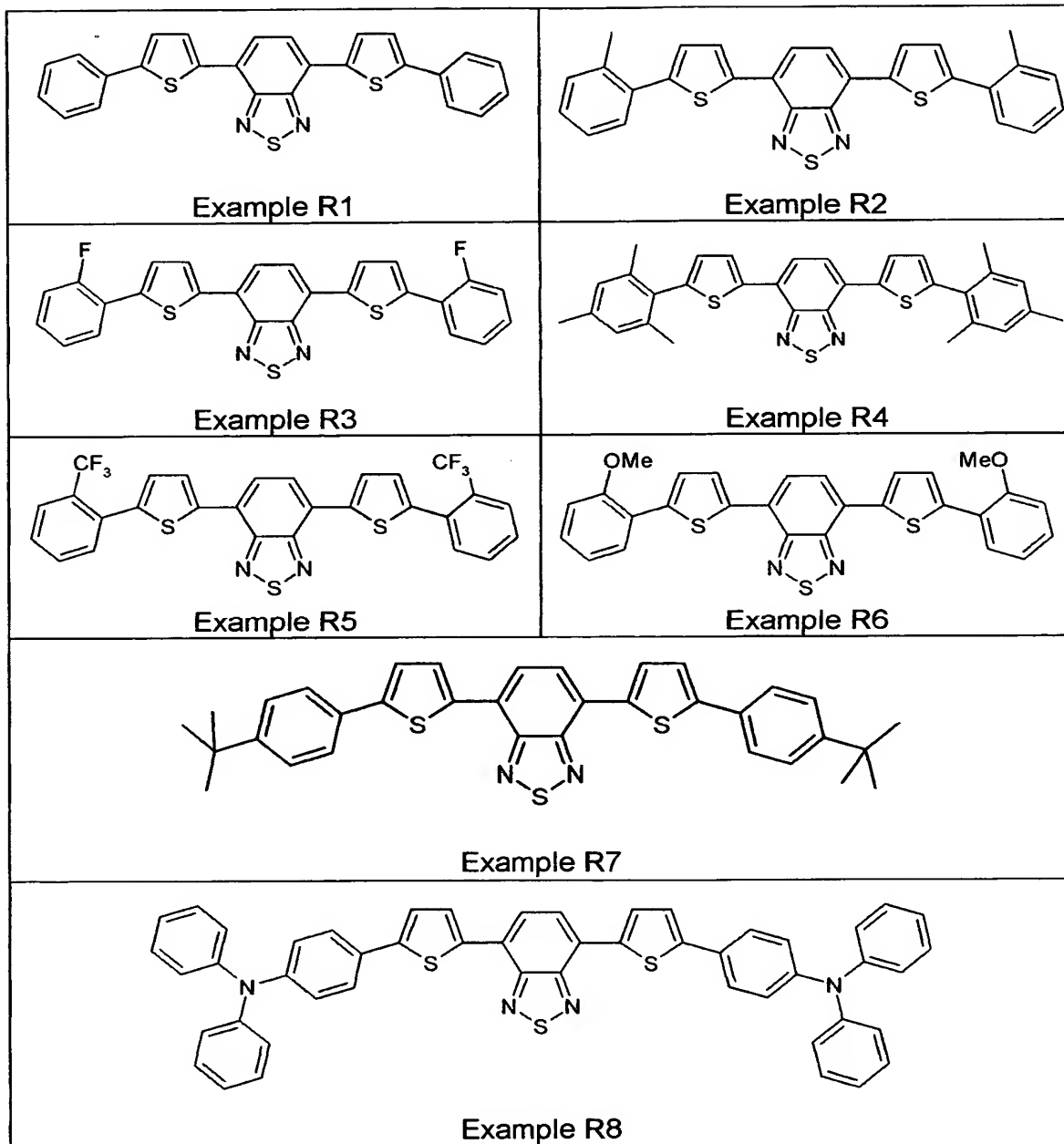
These are likewise part of the present invention.

In order to be used as function material, the compounds containing 2,1,3-benzothiadiazole according to the invention are applied, in the form of a film, to a substrate, generally by known methods familiar to the person skilled in the art, such as vacuum evaporation, evaporation in a stream of carrier gas, or also from solution by

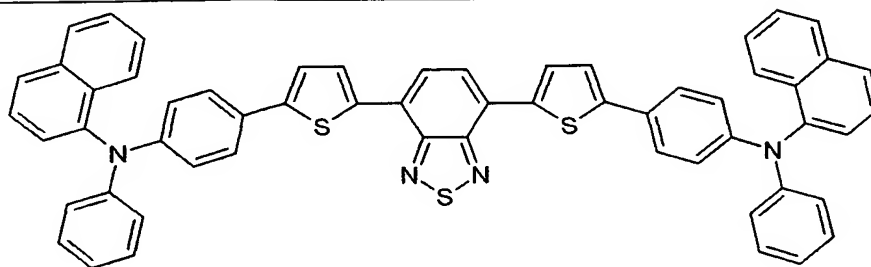
spin coating or using various printing processes (for example ink-jet printing, offset printing, etc.).

Some examples of the compounds containing 2,1,3-benzothiadiazole according to the invention are given below:

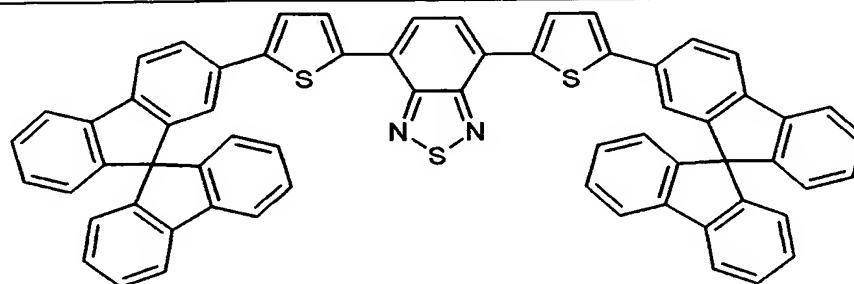
- Examples of orange- to red-emitting compounds containing 2,1,3-benzothiadiazole:



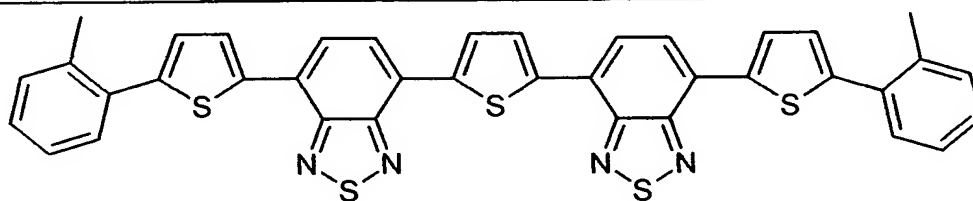




Example R9

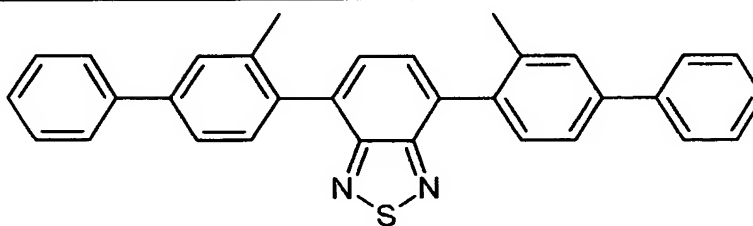


Example R10

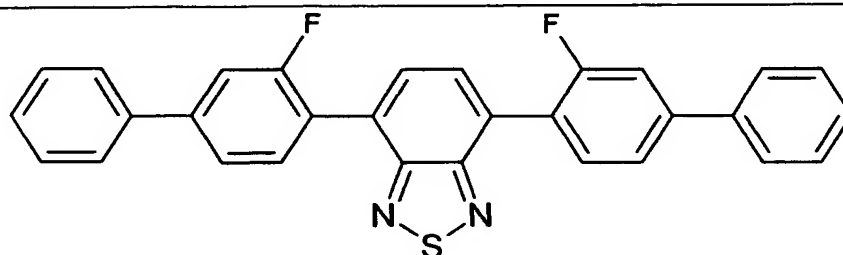


Example R11

- Examples of green- to yellow-emitting compounds containing 2,1,3-benzothiadiazole:

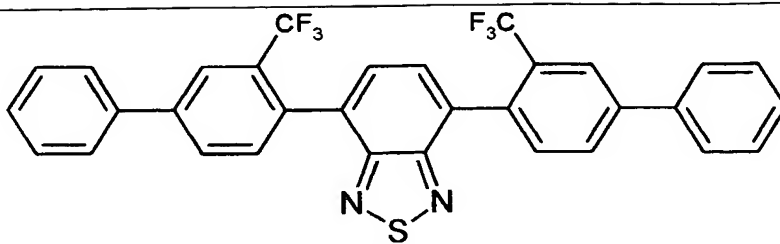


Example G1

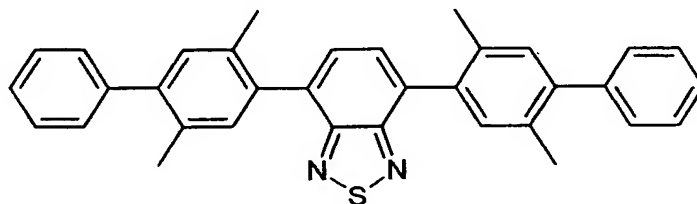


Example G2

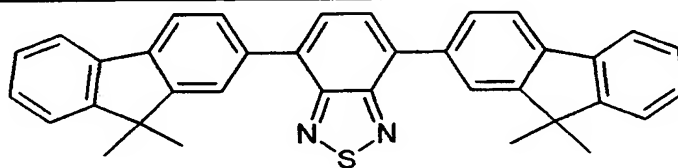
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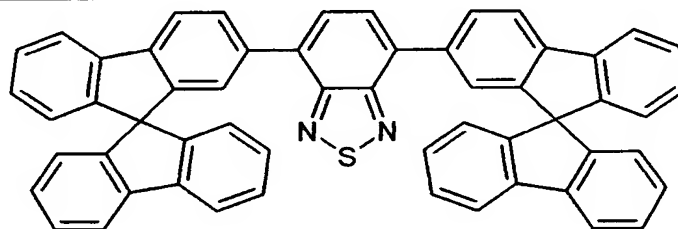
Example G3



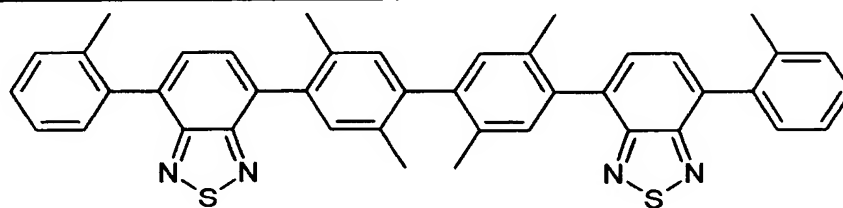
Example G4



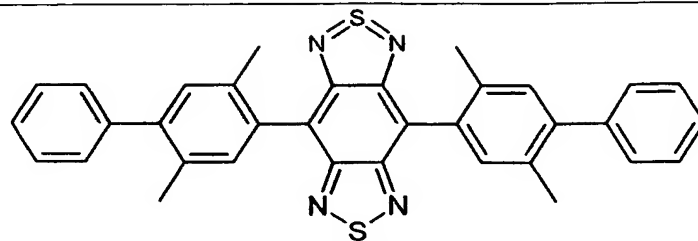
Example G5



Example G6

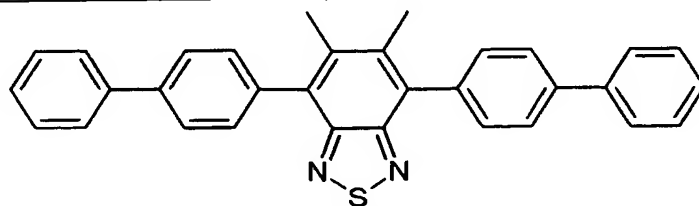


Example G7

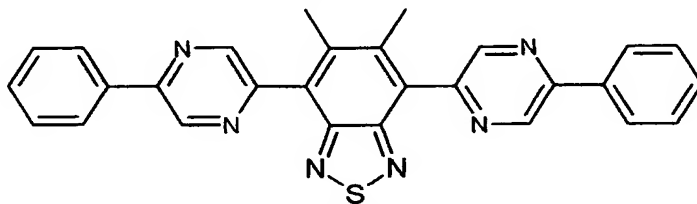


Example G8

17

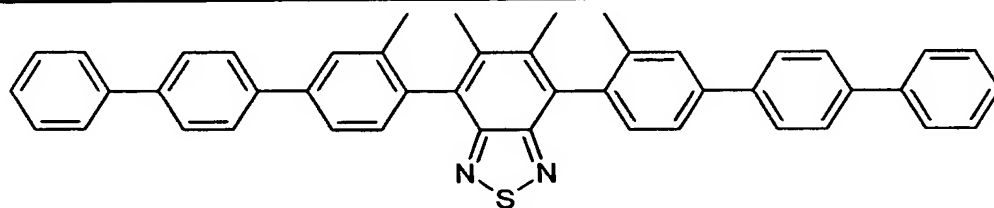


Example G9

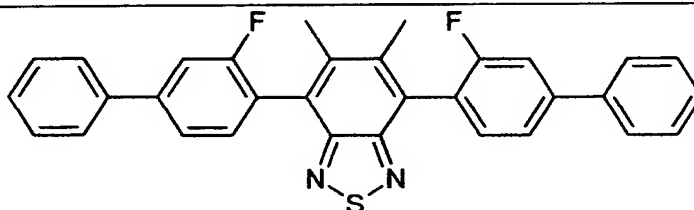


Example G10

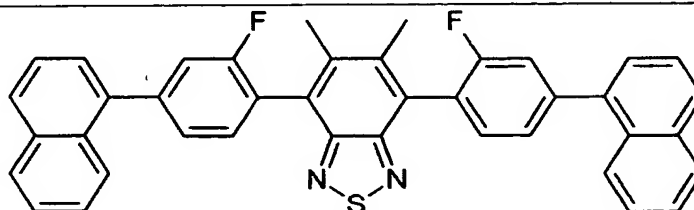
- Examples of dark-blue- to cyan-emitting compounds containing 2,1,3-benzothiadiazole:



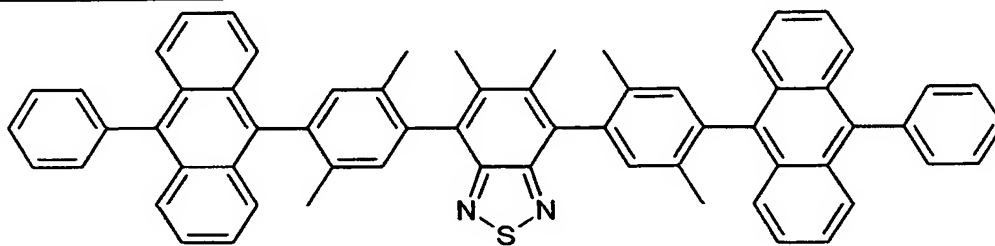
Example B1



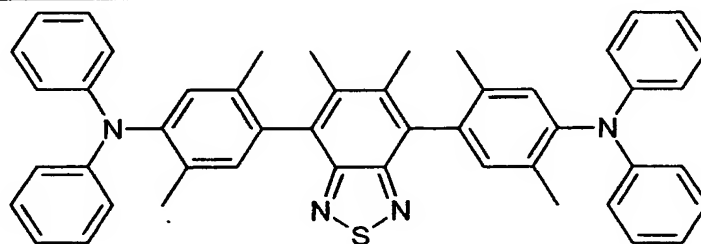
Example B2



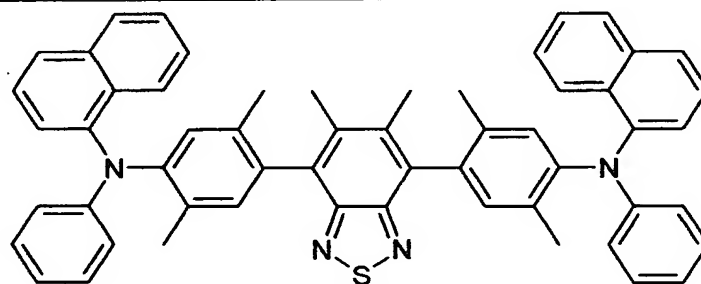
Example B3



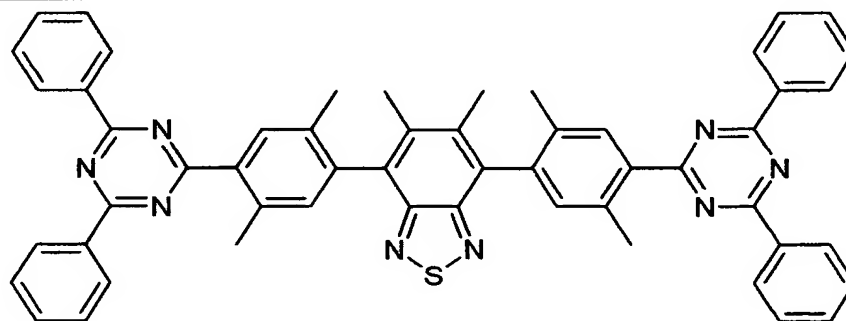
Example B4



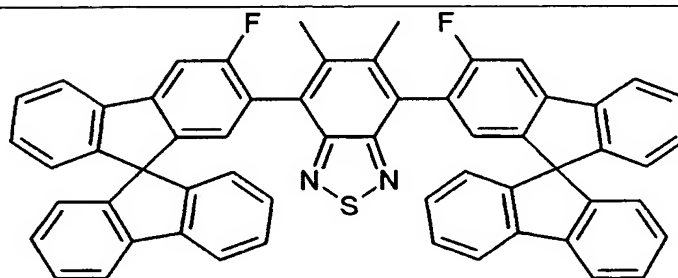
Example B5



Example B6

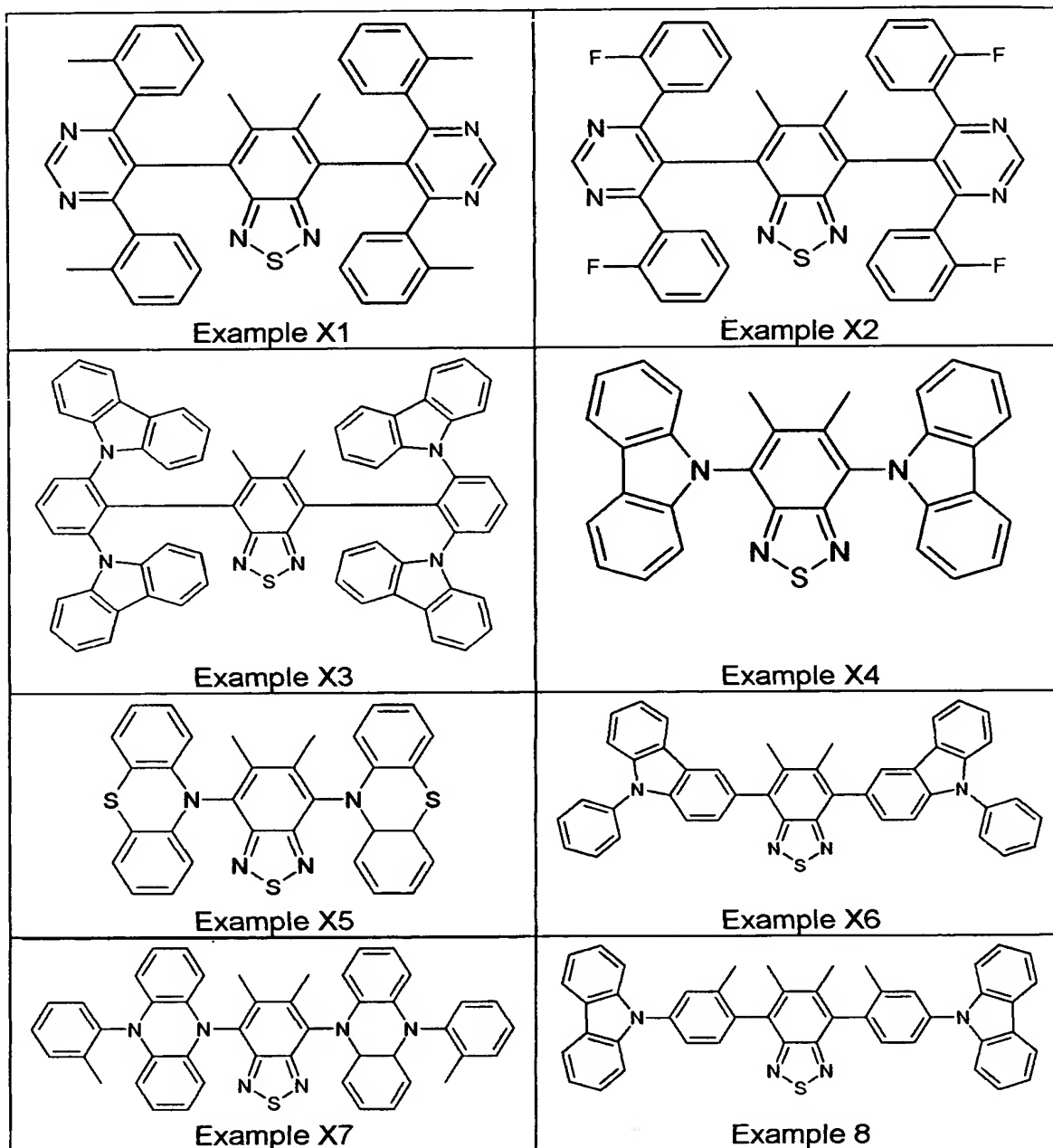


Example B7



Example B8

- Examples of compounds containing 2,1,3-benzothiadiazole which are used as ETL, HBL and as host material in the EML:



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The compounds containing 2,1,3-benzothiadiazole were prepared by standard methods familiar to the person skilled in the art, in particular using palladium-catalysed C-C (for example Suzuki coupling) or C-N coupling reactions (Hartwig-Buchwald coupling), starting from brominated 2,1,3-benzothiadiazoles and aryl-boronic acids or arylamines.

The present invention is explained in greater detail by the following examples, without wishing to be restricted thereto. The person skilled in the art will be able to prepare further derivatives according to the invention from the descriptions without an inventive step.

## 1. Synthesis of compounds containing 2,1,3-benzothiadiazole

The following syntheses were carried out – unless indicated otherwise – under a protective-gas atmosphere. The starting materials were purchased from ALDRICH [2,1,3-benzothiadiazole, N-bromosuccinimide, thiopheneboronic acid, phenylboronic acid, o-tolylboronic acid, o-fluoroboronic acid, potassium phosphate, sodium cyanide, tri-*tert*-butylphosphine, palladium(II) acetate, Pd(PPh<sub>3</sub>)<sub>4</sub>] or from ALFA [4-chloro-2-methylphenylboronic acid] or prepared by literature methods (4,7-dibromo-2,1,3-benzothiadiazole, 4,7-dibromo-5,6-dimethyl-2,1,3-benzothiadiazole: K. Pilgram, M. Zupan, R. Skiles J. Heterocycl. Chem. **1970**, 7, 629).

### 1.1 Synthesis of relevant precursors

#### Example C1: Bis-4,7-(2'-thienyl)-2,1,3-benzothiadiazole

13.52 g (11.7 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> were added to a degassed mixture of 52.92 g (180.0 mmol) of 4,7-dibromo-2,1,3-benzothiadiazole, 60.14 g (470.0 mmol) of thiophene-2-boronic acid, 149.02 g (702.0 mmol) of K<sub>3</sub>PO<sub>4</sub>, 1000 ml of dioxane and 1000 ml of water. After the mixture had been heated at 80°C for 7 h, 4.58 g (93.6 mmol) of NaCN were added. After cooling to room temperature, the aqueous phase was separated off. The organic phase was washed twice with H<sub>2</sub>O and subsequently dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent and recrystallisation of the dark-red solid twice from dioxane, the product was obtained in the form of red needles. The yield – with a purity of > 99.8% (HPLC) – was 43.28 g (144.1 mmol) (80.0%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): [ppm] = 8.11 (dd, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 2H), 7.89 (s, 2H), 7.46 (dd, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 2H), 7.21 (dd, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, 2H).

**Example C2: Bis-4,7-(5'-bromo-2'-thienyl)-2,1,3-benzothiadiazole**

9.51 g (54.0 mmol) of N-bromosuccinimide were added to a solution of 7.72 g (25.7 mmol) of bis-4,7-(2'-thienyl)-2,1,3-benzothiadiazole in 770 ml of chloroform at room temperature and with exclusion of light. The mixture was stirred for 6 h, subsequently concentrated to a volume of 100 ml, 300 ml of ethanol were added, the product was filtered off with suction and washed three times with 100 ml of ethanol. After drying under reduced pressure (70°C, 1 mbar), the residue was recrystallised three times from DMF. The product was obtained in the form of red crystals. The yield – with a purity of > 99.8% (HPLC) – was 10.31 g (22.5 mmol) (87.5%).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): [ppm]= 8.17 (s, 2H), 7.95 (d, <sup>3</sup>J<sub>HH</sub> = 4.2 Hz, 2H), 7.40 (d, <sup>3</sup>J<sub>HH</sub> = 4.2 Hz, 2H).

**Example C3: Bis-4,7-(4-chloro-2-methylphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole**

809 mg (0.70 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> were added to a vigorously stirred, degassed suspension of 91.13 g (283.0 mmol) of 4,7-dibromo-5,6-dimethyl-2,1,3-benzothiadiazole, 125.41 g (736.0 mmol) of 4-chloro-2-methylbenzeneboronic acid and 300.19 g (2832.0 mmol) of Na<sub>2</sub>CO<sub>3</sub> in a mixture of 1800 ml of water and 1800 ml of dioxane, and the mixture was subsequently refluxed for 16 h. After cooling, the precipitated solid was filtered off with suction, washed three times with 300 ml of water and three times with 300 ml of ethanol. After drying, the solid was recrystallised twice from 150 ml of toluene and 260 ml of ethanol. The product was obtained in the form of colourless crystals. The yield – with a purity of > 99.6% (HPLC) – was 98.57 g (238.4 mmol) (84.2%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): [ppm]= 7.28, 7.27 (2 x s, 2H), 7.19, 7.18 (2 x br. s, 2H), 7.06, 7.03 (2 x br. s, 2H), 2.23 (s, 6H), 1.99, 1.98 (2 x s, 6H).

**1.2 Synthesis of red emitters:****Example R1: Bis-4,7-(5'-phenyl-2'-thienyl)-2,1,3-benzothiadiazole**

A degassed mixture of 4.53 g (10.0 mmol) of bis-4,7-(2'-bromo-5'-thienyl)-2,1,3-benzothiadiazole (Example C2), 3.66 g (30.0 mmol) of benzeneboronic acid, 8.92 g

(42.0 mmol) of  $K_3PO_4$  and 1.16 g (1.0 mmol) of  $Pd(PPh_3)_4$  in 400 ml of dioxane and 400 ml of water was heated at 80°C for 7 h. After cooling, 0.49 g (10.0 mmol) of NaCN was added to the mixture, after stirring for 15 min. the aqueous phase was separated off, the organic phase was washed twice with  $H_2O$  and subsequently dried over  $Na_2SO_4$ . After removal of the solvent and recrystallisation twice from DMF, the product was obtained in the form of red needles. The yield – with a purity of > 99.9% (HPLC) – was 4.31 g (9.5 mmol) (95.2%).

$^1H$  NMR (DMSO- $d_6$ , 500 MHz): [ppm]= 8.21 (d,  $^3J_{HH} = 4.0$  Hz, 2H), 8.18 (s, 2H), 7.82 (m, 2H), 7.69 (d,  $^3J_{HH} = 4.0$  Hz, 2H), 7.47 (m, 4H), 7.37 (m, 4H). m.p.: 229°C

#### Example R2: Bis-4,7-(5'(2-methylphenyl)-2'-thienyl)-2,1,3-benzothiadiazole

Procedure analogous to Example R1. Instead of the benzeneboronic acid, 4.08 g (30.0 mmol) of 2-methylphenylboronic acid were employed.

The yield – with a purity of > 99.9% (HPLC) – was 4.37 g (9.1 mmol) (91.0%).

$^1H$  NMR ( $CDCl_3$ , 500 MHz): [ppm]= 8.15 (d,  $^3J_{HH} = 4.0$  Hz, 2H), 7.91 (s, 2H), 7.52 (m, 2H), 7.29 (m, 6H), 7.19 (d,  $^3J_{HH} = 4.0$  Hz, 2H), 2.53 (s, 6H). m.p.: 198°C

#### Example R3: Bis-4,7-(5'(2-fluorophenyl)-2'-thienyl)-2,1,3-benzothiadiazole

Procedure analogous to Example R1. Instead of the benzeneboronic acid, 4.20 g (30.0 mmol) of 2-fluorophenylboronic acid were employed.

The yield – with a purity of > 99.9% (HPLC) – was 4.28 g (7.2 mmol) (72.0%).

$^1H$  NMR ( $CDCl_3$ , 500 MHz): [ppm] = 8.14 (dd,  $^3J_{HH} = 4.0$  Hz,  $^6J_{HF} = 0.67$  Hz, 2H), 7.92 (s, 2H), 7.72 (m, 2H), 7.59 (dd,  $^3J_{HH} = 4.0$  Hz,  $^5J_{HF} = 1.34$  Hz, 2H), 7.21 (m, 6H). m.p.: 193°C

### 1.3 Synthesis of green emitters:

#### Example G6: Bis-4,7-(2-spiro-9,9'-bifluorenyl)-2,1,3-benzothiadiazole

Procedure analogous to Example R1. Instead of the benzeneboronic acid, 10.81 g (30.0 mmol) of spiro-9,9'-bifluorene-2-boronic acid were employed.

The yield – with a purity of > 99.9% (HPLC) – was 5.58 g (7.3 mmol) (73.0%).



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): [ppm] = 7.93 (s, 2H), 7.84 (m, 4H), 7.80 (m, 2H), 7.67 (m, 2H), 7.48 (m, 2H), 7.38 (m, 4H), 7.35 (m, 2H), 7.11 (m, 6H), 6.85 (m, 2H), 6.71 (m, 6H). m.p. > 350°C

#### 1.4 Synthesis of blue emitters:

##### Example B1: Bis-4,7-(2-methylterphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole

243 mg (1.2 mmol) of tri-*tert*-butylphosphine and 225 mg (1.0 mmol) of palladium(II) acetate were added to a vigorously stirred, degassed suspension of 41.34 g (100.0 mmol) of bis-4,7-(4-chloro-2-methylphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole, 55.51 g (280 mmol) of biphenyl-4-boronic acid and 136.84 g (420 mmol) of Cs<sub>2</sub>CO<sub>3</sub> in 1500 ml of dioxane, and the mixture was subsequently refluxed for 16 h. After cooling, 1500 ml of water were added, and the deposited precipitate was washed three times with 300 ml of water and three times with 300 ml of ethanol. After drying, the solid was recrystallised four times from 300 ml of toluene and 100 ml of ethanol. The product was obtained in the form of colourless crystals. The yield – with a purity of > 99.9% (HPLC) – was 53.14 g (81.9 mmol) (81.9%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): [ppm]= 7.88 (m, 4H), 7.69 (m, 4H), 7.61 (m, 4H), 7.47 (m, 4H), 7.37 (m, 2H), 7.26, 7.25 (2 x s, 2H), 7.14, 7.13 (2 x br. s, 2H), 7.09, 7.08 (2 x br. s, 2H), 2.22 (s, 6H), 1.97, 1.96 (2 x s, 6H). m.p.: 281°C

## 2. Production and characterisation of organic electroluminescent devices comprising the compounds according to the invention

LEDs were produced by the general process outlined below. Naturally, this had to be adapted in individual cases to the respective circumstances (for example layer-thickness variation in order to achieve optimum efficiency or colour).

### 2.1 General process for the production of OLEDs

After the ITO-coated substrates (for example glass supports, PET film) have been cut to the correct size, they are cleaned in a plurality of cleaning steps in an ultrasound bath (for example soap solution, Millipore water, isopropanol).

For drying, they are blown with an N<sub>2</sub> gun and stored in a desiccator. Before the vapour deposition with the organic layers, they are treated with an ozone plasma

unit for about 20 minutes. It can be recommended to use a polymeric hole-injection layer as the first organic layer. This is generally a conjugated, conductive polymer, such as, for example, a polyaniline derivative (PANI) or a polythiophene derivative (for example PEDOT, BAYTRON P™ from BAYER). This is then applied by spin coating.

The organic layers are applied one after the other by vapour deposition in a high-vacuum unit. The layer thickness of the respective layer and the vapour deposition rate is monitored or adjusted here via a vibrating quartz crystal.

It is also possible – as described above – for individual layers to consist of more than one compound, i.e. in general for a host material to be doped with a guest material. This is achieved by co-evaporation from two or more sources.

Electrodes are also applied to the organic layers. This is generally carried out by thermal evaporation (Balzer BA360 or Pfeiffer PL S 500). The transparent ITO electrode is subsequently contacted as anode and the metal electrode (for example Ca, Yb, Ba/Al) as cathode, and the device parameters are determined.

## 2.2 Process for the production of red OLEDs

### Example 1: Red OLED comprising emitter material according to Example R1

A red-emitting OLED having the following structure was produced analogously to the above-mentioned general process:

PEDOT	20 nm (spin-coated from water; PEDOT purchased from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene])
MTDATA	20 nm (vapour-deposited; MTDATA purchased from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine)
S-TAD	20 nm (vapour-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene)
AlQ <sub>3</sub>	30 nm (vapour-deposited; AlQ <sub>3</sub> purchased from SynTec; tris-(quinoxalinato)aluminium(III)) and doped with
R1	10% by weight (vapour-deposited; bis-4,7-(5'-phenyl-2'-thienyl)-2,1,3-benzothiadiazole prepared as described in Example R1)

AlQ <sub>3</sub>	10 nm (vapour-deposited; AlQ <sub>3</sub> purchased from SynTec; tris(quinoxalinato)aluminium(III))
Ba	10 nm as cathode
Ag	100 nm as cathode-protection layer

This **non**-optimised OLED was characterised by standard methods, the measured characteristic data are shown in Figures 1-3. Besides the flatness of the efficiency curve, which means that high efficiencies are still achieved even at very high brightnesses (for example 10,000 Cd/m<sup>2</sup>), the excellent lifetime of this OLED is of major advantage.

### 2.3 Process for the production of blue OLEDs

#### Example 2: Blue OLED comprising emitter material according to Example B1

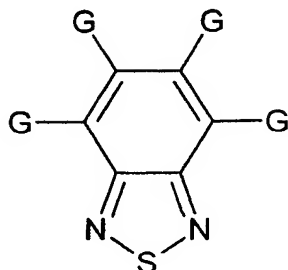
A blue-emitting OLED having the following structure was produced analogously to the above-mentioned general process:

PEDOT	20 nm (spin-coated from water; PEDOT purchased from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene])
MTDATA	20 nm (vapour-deposited; MTDATA purchased from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine)
S-TAD	20 nm (vapour-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene)
S-DPVBi	30 nm (vapour-deposited; S-DPVBi prepared by the method of H. Spreitzer, H. Schenk, J. Salbeck, F. Weissoertel, H. Riel. W. Ries, Proceedings of SPIE, <b>1999</b> , Vol. 3797; 2,2',7,7'-tetrakis(2,2'-diphenylvinyl)spiro-9,9'-bifluorene) and doped with 10% by weight (vapour-deposited; 5,6-dimethylbis-4,7-(2,5-dimethylphenyl)-2,1,3-benzothiadiazole prepared as described in Example B1), doped into the above S-DPVBi layer
AlQ <sub>3</sub>	10 nm (vapour-deposited: AlQ <sub>3</sub> purchased from SynTec; tris(quinoxalinato)aluminium(III))

Ba	10 nm as cathode
Ag	100 nm as cathode-protection layer

This **non**-optimised OLED was characterised by standard methods, the measured characteristic data are shown in Figures 4 and 5. Besides the colour, an enormous advantage of this OLED is the flatness of the efficiency curve, which means that very high efficiencies are still achieved even at very high brightnesses (for example 10,000 Cd/m<sup>2</sup>). This is of crucial importance, in particular, for use in passive matrix-driven displays.

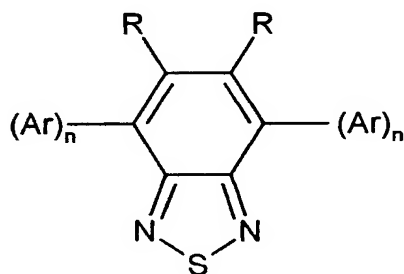
1. Compounds containing at least one structural unit of the formula (I)



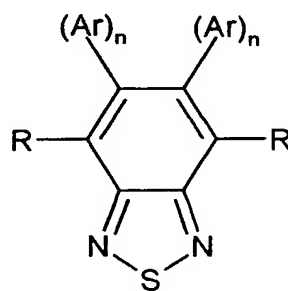
Formula (I)

characterised in that the group G corresponds to hydrogen, fluorine and/or an organic radical, the compounds belong to the idealised point group  $S_n$ ,  $C_n$ ,  $C_{nv}$ ,  $C_{nh}$ ,  $D_n$ ,  $D_{nh}$  or  $D_{nd}$  where  $n = 2, 3, 4, 5$  or  $6$ , the molecular weights are in the range from 450 g/mol to 5000 g/mol, the melting points are above a temperature of  $190^\circ\text{C}$ , and with the proviso that no macrocycle is present.

2. Compounds of the formula (II) and (III) according to Claim 1,



Formula (II)



Formula (III)

where the symbols and indices have the following meaning:

R is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent  $\text{CH}_2$  groups may be replaced by -O-, -S-, - $\text{NR}^1$ -, or - $\text{CONR}^2$ - and in which one or more H atoms may be replaced by F;

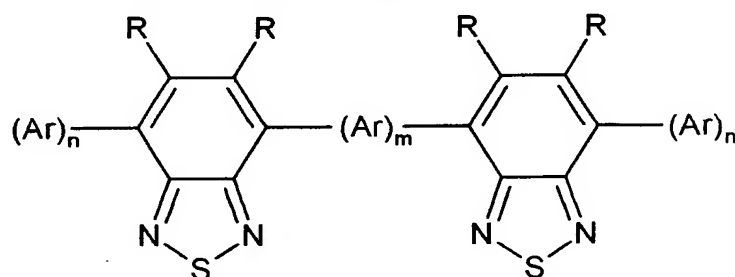
Ar is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or

more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;

$R^1, R^2$  are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

n is equal to 1 to 10, preferably 1 to 6, particularly preferably 1, 2 or 3.

3. Compounds of the formula (IV) according to Claim 1,



**Formula (IV)**

where the symbols and indices have the following meaning:

R is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent  $CH_2$  groups may be replaced by  $-O-$ ,  $-S-$ ,  $-NR^1-$ , or  $-CONR^2-$  and in which one or more H atoms may be replaced by F;

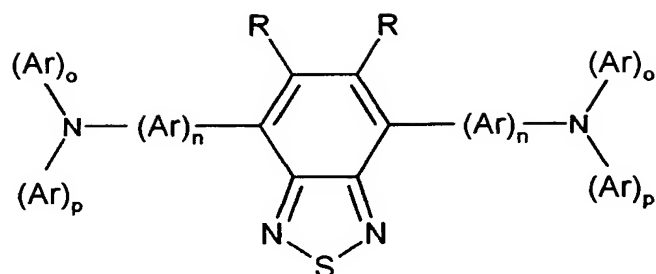
Ar is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;

$R^1, R^2$  are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

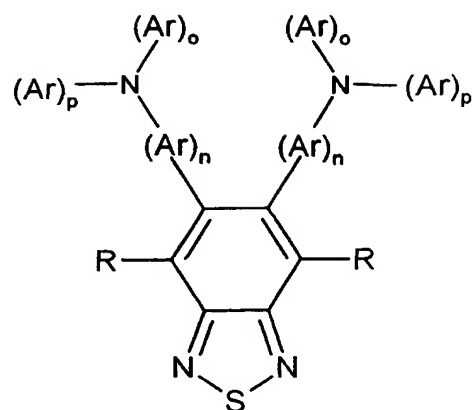
m is equal to 0 to 4, preferably 1 or 2;

n is equal to 1 to 10, preferably 1 to 6, particularly preferably 1, 2 or 3.

4. Compounds of the formula (V) and (VI) according to Claim 1,



Formula (V)

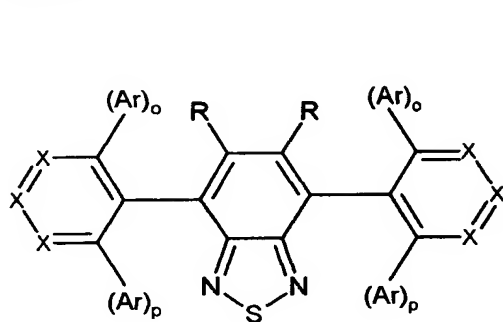


Formula (VI)

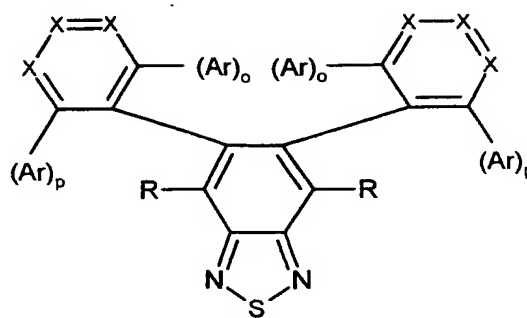
where the symbols and indices have the following meaning:

- R** is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -NR<sup>1</sup>-, or -CONR<sup>2</sup>- and in which one or more H atoms may be replaced by F;
- Ar** is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;
- R<sup>1</sup>, R<sup>2</sup>** are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;
- n** is equal to 1 to 10, preferably 1 to 6, particularly preferably 1, 2 or 3.
- o** is equal to 1 to 3, preferably 1;
- p** is equal to 1 to 3, preferably 1.

5. Compounds of the formula (VII) and (VIII) according to Claim 1,



Formula (VII)



Formula (VIII)

where the symbols and indices have the following meaning:

X is, identically or differently on each occurrence, C(Ar), CR or N;

R is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -NR<sup>1</sup>-, or -CONR<sup>2</sup>- and in which one or more H atoms may be replaced by F;

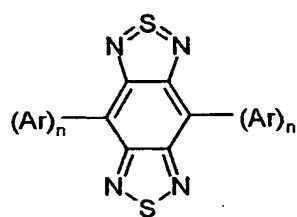
Ar is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;

R<sup>1</sup>, R<sup>2</sup> are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

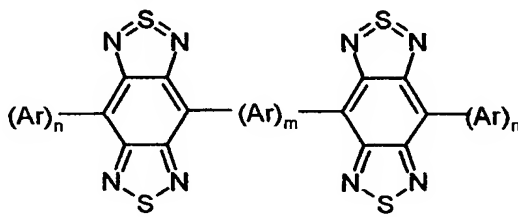
o is equal to 1 to 3;

p is equal to 1 to 3.

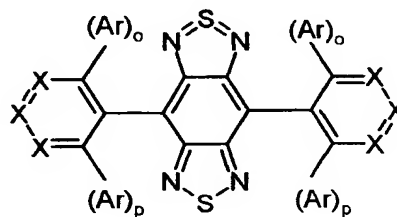
6. Compounds of the formula (IX), (X) and (XI) according to Claim 1,



Formula (IX)



Formula (X)



Formula (XI)



where the symbols and indices have the following meaning:

X is, identically or differently on each occurrence, C(Ar), CR or N;

R is, identically on each occurrence, H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -S-, -NR<sup>1</sup>-, or -CONR<sup>2</sup>- and in which one or more H atoms may be replaced by F:

Ar is, identically or differently on each occurrence, an aryl or heteroaryl group having 3 to 30 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, may together in turn define a further mono- or polycyclic ring system;

R<sup>1</sup>, R<sup>2</sup> are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

m is equal to 0 to 4, preferably 1 or 2;

n is equal to 1 to 10, preferably 1 to 6, particularly preferably 1, 2 or 3;

o is equal to 1 to 3;

p is equal to 1 to 3.

7. Compounds according to one or more of Claims 1 to 6, characterised in that the radical Ar stands for benzene, toluene, xylene, fluorobenzene, difluorobenzene, biphenyl, 1,2- or 1,3- or 1,4-terphenyl, tetraphenyl, naphthyl, fluorene, 9,9'-spiro-bifluorene, phenanthrene, anthracene, 1,3,5-triphenylbenzene, pyrene, perylene, chrysene, triptycene, [2.2]paracyclophan, pyridine, pyridazine, 4,5-benzopyridazine, pyrimidine, pyrazine, 1,3,5-triazine, pyrrole, indole, 1,2,5- or 1,3,4-oxadiazole, 2,2'- or 4,4'-bipyridyl, quinoline, carbazole, 5,10H-dihydrophenazine, 10H-phenoxazine, phenothiazine, xanthene, 9-acridine, furan, benzofuran, thiophene or benzothio-phene.

8. Use of the compounds according to one or more of Claims 1 to 7 in organic electroluminescent and/or electrophosphorescent devices.

9. Use of the compounds according to one or more of Claims 1 to 7 as emission layer (EML), as host material in electroluminescent and/or electrophosphorescent devices, as electron-transport layers (ETLs) and/or hole-blocking layers (HBLs).

5 10. Use of the compounds according to one or more of Claims 1 to 7 as electron-transport material in electrophotography, as electron-acceptor or -transport material in photovoltaic devices, such as organic photodetectors or organic solar cells, as charge-transport material in organic ICs (organic integrated circuits), as charge-transport material and/or dopant in organic field-effect transistors (OTFTs), as  
10 charge-transport material and/or dopant in organic thin-film transistors and in organic solid-state lasers.

11. Electronic component comprising at least one compound according to one or more of Claims 1, 2, 3, 4, 5 and/or 6.

## 2,1,3-Benzothiadiazoles

5       The present invention describes novel compounds containing 2,1,3-benzothia-  
diazole. Compounds of this type can be employed as active components (= function  
materials) in a number of different applications which can be ascribed to the elec-  
tronics industry in the broadest sense.

10       The compounds according to the invention are described by the formulae (I), (II),  
(III), (IV), (V), (VI), (VII), (VIII), (IX), (X) and (XI).

Figure 1: Characteristic data of the OLEDs according to Example 1

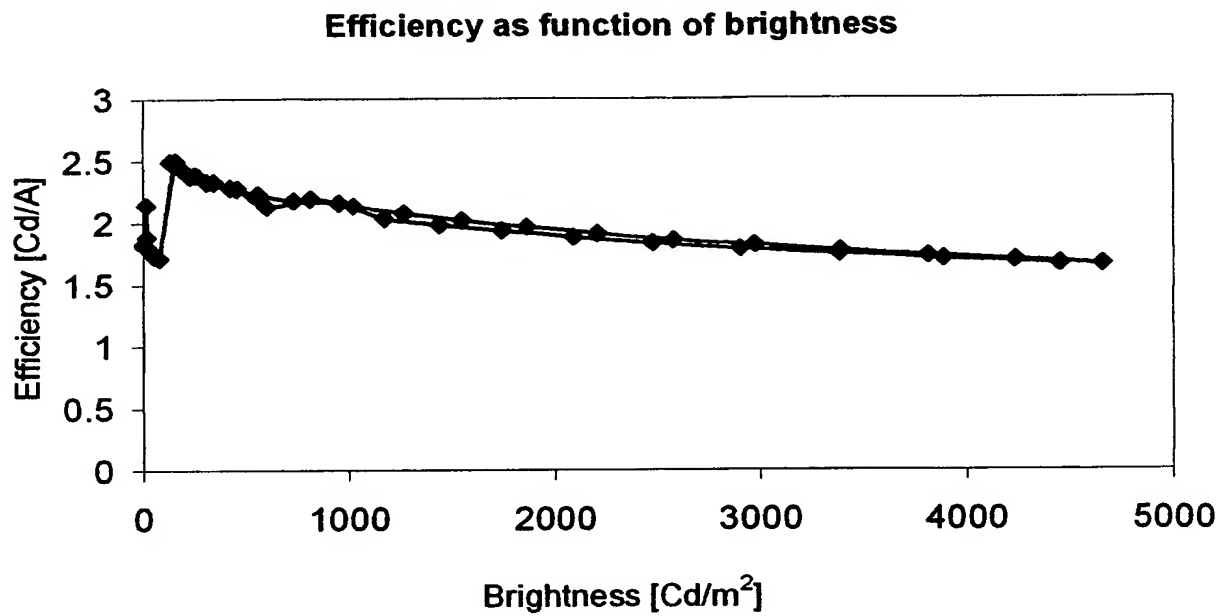
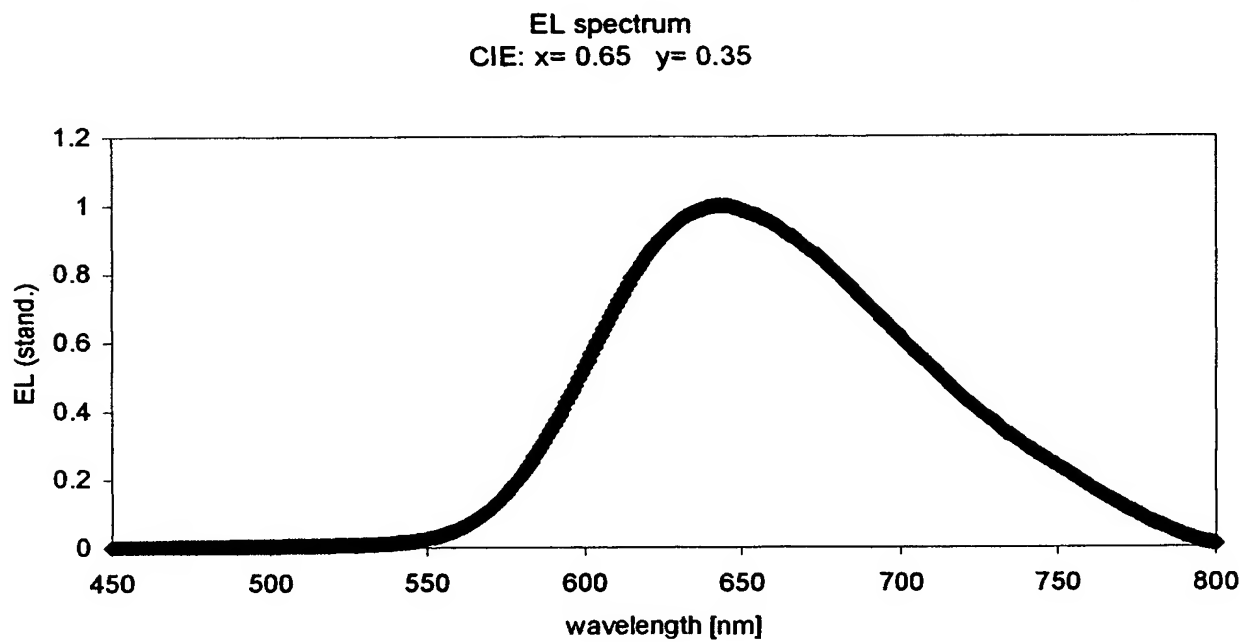


Figure 2: Characteristic data of the OLEDs according to Example 1



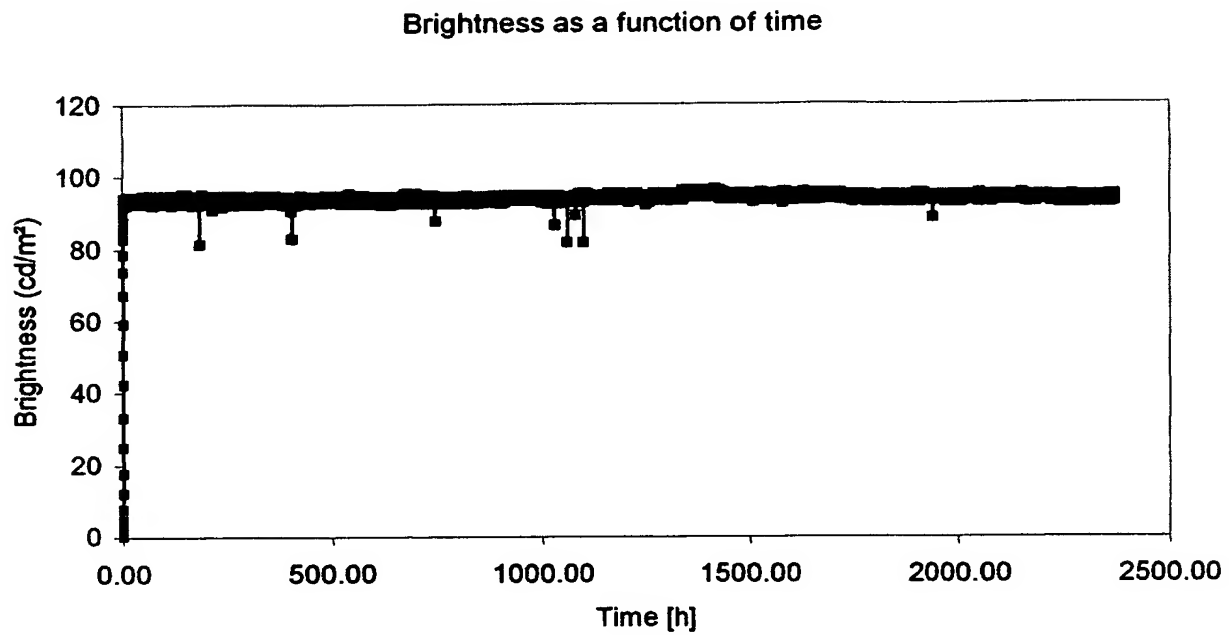
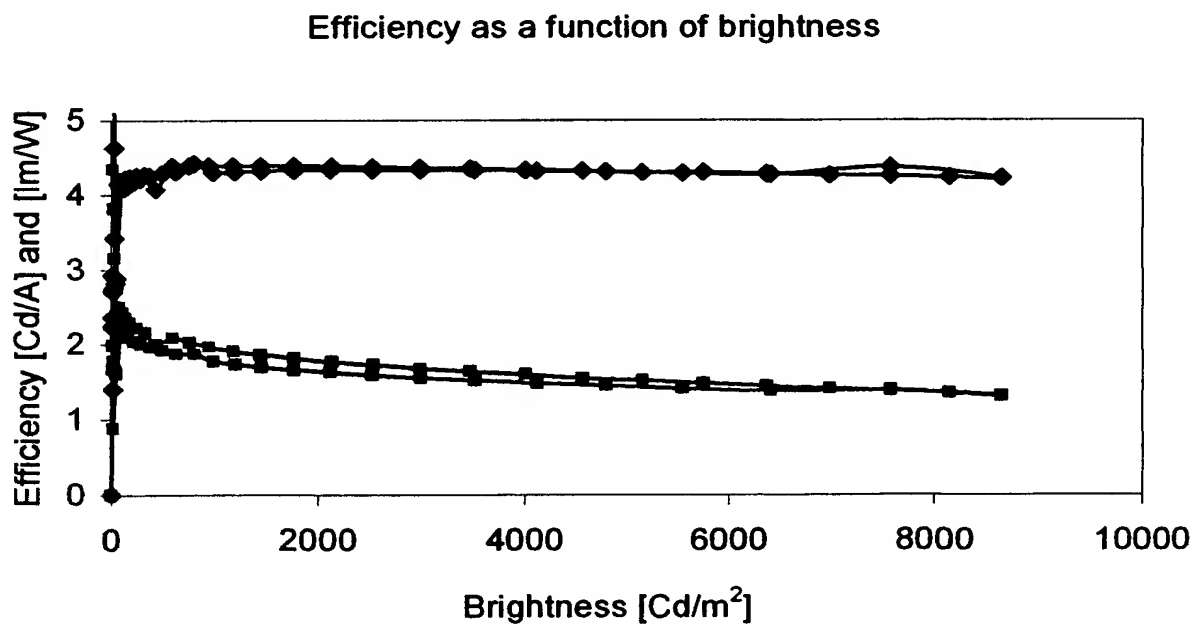
**Figure 3: Characteristic data of the OLEDs according to Example 1****Figure 4: Characteristic data of the OLEDs according to Example 2**

Figure 5: Characteristic data of the OLEDs according to Example 2

